# **MolExplorer**<sup>TM</sup>

Program for the Calculation and Display of Molecular Spectra



## **Instruction Manual**

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### 1. Introduction

The MolExplorer is a program for fast computation and display of molecular spectra on a PC Microsoft Windows® platform. The program takes advantage of a database, in which the relevant parameters for the calculation of a spectrum are stored. Two versions of the MolExplorer with an identical program platform and graphical user interface but applying different databases are delivered:

- The MolExplorer-H uses the data of the well known HITRAN08 database [1], in which more than 2 Mio spectral lines of the 42 most prominent molecules in the atmosphere are stored. HI-TRAN is an acronym for high-resolution transmission molecular absorption database and is a compilation of spectroscopic parameters to predict and simulate the transmission and emission of light in the atmosphere [1-5].
- The MolExplorer–G relies on the database GEISA-03 [6,7] (Gestion et Etude des Informations Spectroscopiques Atmosphériques: Management and Study of Atmospheric Spectroscopic Information). This database contains more than 1.6 Mio transitions of 42 molecules which are of interest in studies of the terrestrial as well as other planetary atmospheres.

Both versions calculate the molecular absorption and model the attenuation of radiation in the atmosphere or under laboratory conditions. Within seconds they provide survey spectra from mm-waves up to the ultra violet as well as selected parts with highest spectral resolution, and this for the most relevant gases and pollutants in the atmosphere.

The user only has to specify the molecules or isotopologues of interest, the respective partial pressures and the spectral range, perhaps additionally the temperature. All further steps are accomplished by the MolExplorer.

The present version includes the following new features:

- Direct comparison of spectra calculated from Hitran- or Geisa-data is possible when operating and displaying simultaneously both versions on the screen.
- Also an import of spectral data from a measurement or another calculation can be performed to compare and to fit the data to a spectrum calculated from the HITRAN08 or GEISA-03 database.
- A further broadening of the spectra which may be caused by the limited resolution of a spectrometer, can be simulated by folding the spectrum with an instrument function.
- Additionally, the propagation of radiation under the influence of Mie scattering and free-spacedamping through a standard atmosphere, which is changing with altitude in its pressure and temperature, can be calculated.

The program was developed at the Helmut-Schmidt-University – University of the Federal Armed Forces Hamburg – by H. Harde and J. Pfuhl.

### 2. Installation of the Program

The MolExplorer is delivered on a CD/DVD together with some additional files required to run the program. Also included are the HITRAN08 and GEISA-03 databases. Updates of the Hitran-file can be downloaded from the HITRAN homepage <u>http://www.cfa.Harvard.edu/HITRAN/hitrandata04/</u>, for the Geisa-file from the homepage <u>http://ara.Imd.polytechnique.fr/</u> of the Atmospheric Radiation Analysis Group. Going to these web-sites you will be prompted for a Username and Password. The latter are obtained by filling out a request form or sending an email. Typically within one week you will get the login data.

It is recommended to install the MolExplorer and the database files on a hard drive for fast retrieval of the data. Copy the folder MolExplorer e.g., as subdirectory of c:\Programs.

The folder MolExplorer contains the two programs MolExplorer-H.exe and MolExplorer-G.exe as well as the files Hitran08.par, Hitran08Index.dat, Hitran08Info.txt, Hitran08Job.txt, Hitran08Pointer.txt, geisa2003\_line, GEISA-03Index.dat, GEISA-03Info.txt, GEISA-03Job.txt, GEISA-03Pointer.txt and parsum.dat.

**Operating System:** Microsoft Windows 2000 or higher. Required file space ca. 1 GB. Hardcopy output to all regular printers. The program is presently not network adapted.

### 3. Operation

The program platform consists of a graphical user interface (lower part of the screen) and a display area (upper part) for the calculated spectra.

From this window all operations of the MolExplorer are controlled. The lower right part contains the input fields for up to ten gases, the zoom control and logarithmic display function for the spectrum. At the left hand side are found all other control elements necessary for a compilation.

The **MolExplorer–H** takes advantage of the database HITRAN08 [1, 5], which contains the spectral data of 42 atmospheric gases and pollutants (see Table 1) with 97 isotopic species. This database includes about 2 Mio lines with classification of the transitions and all relevant line parameters. The covered spectral range extends from the radio-wave to the ultraviolet region.

Molecule Symbol	Hitran Lines	Geisa Lines	Molecule Symbol	Hitran Lines	Geisa Lines
CF₄	60033		HF	107	107
CH₃Br	36911		н	806	806
CH₃CI	31119	18344	HNO <sub>3</sub>	271166	171504
CH₃CN	3572		HOBr	4358	
CH₃D		35518	HOCI	16276	17862
CH₃OH	19899		HO <sub>2</sub>	38804	38804
CH₄	251440	216196	H₂CO	2702	2701
со	4477	13515	H₂O	63197	58726
CO <sub>2</sub>	62913	76826	H <sub>2</sub> O <sub>2</sub>	100781	100781
COF <sub>2</sub>	70601	83750	H₂S	20788	20788
$C_2H_2$	3517	3115	NH <sub>3</sub>	29084	29082
C <sub>2</sub> H <sub>4</sub>	12978	12978	NO	102280	99123
C₂H <sub>6</sub>	4749	14981	NO⁺	1206	
$C_2N_2$		2577	NO <sub>2</sub>	104223	104224
C₃H₄		3390	N <sub>2</sub>	120	120
C₃H <sub>8</sub>		8983	N₂O	47835	26681
C <sub>4</sub> H <sub>2</sub>		1405	0	2	
CIO	7230	7230	OCS	19920	24922
CIONO <sub>2</sub>	32199 <sup>14</sup>	32199	ОН	42373	42866
GeH₄		824	<b>O</b> <sub>2</sub>	6428	6290
HBr	1293	1294	<b>O</b> <sub>3</sub>	311481	319248
HCN	4253	2550	PH <sub>3</sub>	11790	11740
HC₃N		2027	SF <sub>6</sub>	22901 <sup>14</sup>	11520
нсоон	24808	3388	SO <sub>2</sub>	38853	38853
HCI	613	533			

Table 1: List of molecules with the number of transitions

The **MolExplorer–G** uses the database GEISA-03 [6,7], in which the transition parameters of 42 molecules (see also Table 1) and 98 isotopic species are stored. This database consists of more than 1.66 Mio lines. Both databases cover 49 gases of the terrestrial and other planetary atmospheres.

### **3.1 Selection of Molecules**

The MolExplorer control panel contains 10 fields provided to select molecules by clicking on a dropdown menu. The molecules then appear in alphabetic order and can be selected from this list. Up to 10 different gases can be activated in this way for a computation.



### 3.2 Isotopologues and Isotopomers

Another drop-down menu can be opened to choose between different isotopologues and isotopomers or the natural isotopic mixture.

Isotopologues are molecular entities that only differ in their isotopic composition (e.g. <sup>14</sup>N<sup>14</sup>N<sup>16</sup>O and <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O), while isotopomers have identical isotopic atoms, but at different positions (e.g. <sup>16</sup>O<sup>16</sup>O<sup>18</sup>O and <sup>16</sup>O<sup>18</sup>O<sup>16</sup>O). For further identification the AFGL shorthand notation, e.g. for <sup>14</sup>N<sup>14</sup>N<sup>16</sup>O, <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O and <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O the AFGL abbreviated code 446, 456 and 546 is applied.

All isotopologues and isotopomers used in the two databases are listed in Table 2 together with their natural abundances (see also http://cfa-www.harvard.edu/hitran/molecules.html). The second column in Table 2 indicates, which of the isotopic species are found in the databases (B - both, H - Hitran, G - Geisa). If the abbreviation of the isotopologues or isotopomers in Geisa differs from that of Hitran, the respective code is also listed in column 4.



### 3.3 Partial Pressure - Concentration

With the choice of the molecule the default parameters for the isotope and partial pressure are set to *natural mixture* and *1 hPa*. The isotope is selected by the drop-down menu, the pressure is changed by typing in another value. If the natural mixture of the gas is used, the displayed pressure represents the sum over all isotopologues of the molecule, e.g., for  $CO_2$  the partial pressures of 626, 636, 628, 627, 638, 637, 828 and 728 weighted according to their natural abundances.

If one specific isotopologue is selected, the pressure is only valid for this component.

Sometimes it may be advantageous to distinguish between spectra of different isotopes of the same molecule. Then for each isotopologue another field is provided, e.g., the first line for  $CO_2 - 626$  at a partial pressure of 1 hPa, the second line for  $CO_2 - 636$  at 1 hPa etc. If you want to compute the spectra in relation to their natural abundances, click on the button NA (natural abundance) and the corresponding pressure is multiplied by the abundance of this isotope. The new partial pressure of  $CO_2 - 626$  now is 0.9842 hPa, that of  $CO_2 - 636$  is 0.01106 hPa, and that of  $CO_2 - 628$  is 0.003947 hPa.

Table 2: Molecules with isotopologues and isotopic abundances used in the HITRAN database [Ref. 8]

Molecule	Db	Isotopo- logue	Abundance	Molecule	Db	Isotopo- Iogue	Abundance
CF₄	H	29	0.98889	HOBr	н	169	0.5056
CH₃Br	н	219	0.500995			161	0.4919
		211	0.487433	носі	В	165	0.75579
CH₃CI	В	215	0.74894			167	0.24168
		217	0.23949	HO <sub>2</sub>	В	166	0.995107
	H C	2124	0.0006158	H-CO	в	126	0.98624
	H	212	0.98593	11200	D	128	0.0119776
		211	0.98827			161	0.997317
Сн₄	В	311	0.01110			181	0.00199983
	н	212	0.00061575		_	171	0.000372
		212	0.08654	H₂O	В	162	0.00031069
		20	0.01108			192	0.00031009
		20	0.01100			172	0.00000023
со	В	20	0.0019762		<b>D</b>	172	0.00000110
		27	0.000366		D	1001 100	0.994952
		38	0.00002222		-	121	0.94988
		37	0.00000413	H₂S	в	141	0.04214
		626	0.98420			131	0.007498
		636	0.01106	NH₃	В	4111 411	0.9958715
		628	0.0039471			5111 511	0.0030613
<u></u>	В	627	0.000734	NO	Р	40	0.993974
		638	0.00004434	NO	D	56	0.0036543
		637	0.00000825	NO <sup>†</sup>		48	0.00199312
		828	0.0000039573	NO	н	46	0.993974
		728	0.00000147	NO <sub>2</sub>	В	646	0.991616
	G	838	0.00000004448	N <sub>2</sub>	В	44	0.9926874
COF <sub>2</sub>	В	269	0.98654			446	0.990333
C <sub>2</sub> H <sub>2</sub>	в	1221 221	0.97760		-	456	0.0036409
		1231 231	0.02197	N <sub>2</sub> O	в	546	0.0036409
C <sub>2</sub> H4	в	221 211	0.9773			448	0.00198582
-24	_	231 311	0.02196			447	0.000369
C.H.	В	1221 226	0.97699	0	Н	6	0.997628
C2H6	G	236	0.01098			622	0.93739
C <sub>2</sub> N <sub>2</sub>	G	224	0.9708			624	0.04158
C₃H₄	G	341	0.9664		В	632	0.01053
C <sub>2</sub> H <sub>2</sub>	G	221	0.9658	005		623	0.007399
C₄H₂	G	211	0.956			822	0.001880
- 4- 12	-	56	0.75591		G	634	0.0004672
CIO	в	76	0 24172		-	61	0 997473
		5646 564	0.74957	он	в	81	0.00200014
CIONO <sub>2</sub>	В	7646 764	0.23070	0.11	2	62	0.00200014
	0	1040 704	0.25970			66	0.00013337
GeH <sub>4</sub>	G	411	0.5092		Р	00	0.995262
HBr	В	19	0.30678	02	Б	66	0.00399141
		11	0.49306			67	0.000742
	-	124	0.98511			666	0.992901
HCN	В	134	0.01107	_	<b>_</b>	668	0.00398194
	_	125	0.0036217	03	D	686	0.00199097
HC₃N	G	124	0.9633			667	0.000740
нсоон	В	126 261	0.983898			676	0.000370
нсі	В	15	0.757587	PH <sub>3</sub>	В	1111 131	0.99953283
		17	0.242257	SF <sub>6</sub>	В	29	0.95018
HF B 19 0.9998		0.99984425	SO D		626	0.94568	
н	В	17	0.99984425			646	0.04195
HNO <sub>3</sub>	В	146	0.989110				

In addition to the partial pressures of the selected molecules a buffer gas pressure can be specified. It accounts for the surrounding air pressure with a default value of *1013 hPa*. It is set to zero or to normal air pressure by clicking on the left or right buttons of the buffer gas field or feeding in a new value.

The partial pressures may be changed to concentrations by clicking on the respective checkbox *Concentration*. At an air pressure of 1013 hPa the display for  $CO_2$  - 626 then changes to 970.612 ppm that of  $CO_2$  - 636 to 10.907 ppm, and that of  $CO_2$  - 628 to 3.8925 ppm, while the display for the buffer gas changes to the total pressure.

This option has the advantage that small pollutions in the atmosphere or in another buffer gas can directly be specified in *ppm*-units.

-X-Axis Maximal Bange	
4.4	X: 4.48834 μm
5	Y: 0.0 cm-1   Partial Pressure
Scale C 1/cm	Max: 52.6 cm-1 C Concentration
• um	Lines: 911 out of 911 🔽 Marker
C TH <sub>2</sub>	Display-Modus Buffer Gas [hPa]
Parfile Data	Absorp-Coeff.
Read Import	Min. Intens: Temperature [K]
Write Fit	U.U N 236.0 N
	Channels Path Length [cm] Response Time
Export Data	32768 <u>- On 10.00</u> 10 1

### 3.4 Spectral Range

For any calculation of a spectrum the start and stop values have to be determined. The abscissa can be chosen in wavenumbers  $[cm^{-1}]$ , in frequencies [THz] or wavelengths  $[\mu m]$ . The default configuration starts with the wavelength scale. A click on the respective radio button opens a sub-window to key in these values. Having entered these data, the MolExplorer is ready for a first run.

### Line Retrieval

Use a start wavelength of 1.9  $\mu$ m and a stop wavelength of 2.1  $\mu$ m, confirm with OK and press the Check button at the lower edge of the control environment.

The blue graphic screen changes to white and shows a list of the selected molecules and specified isotopologues with the number of found lines (in this example for the Hitran case: 14305 from 128170 lines for the isotope 626, 5378 from 49777 for 636, and 5856 from 79958 for 628; for the Geisa case: 3378 from 32692 for isotope 626, 761 from 11122 for 636, and 999 from 17417 for 628). This number of lines represents all lines found within an interval given by the specified range as well as one quarter of the spectral width to shorter and higher wavelengths. Also the partial pressures are displayed.

### Display

Clicking on the *Calculate* button the computed absorption spectrum is displayed. In the Hitran case it consists of 25539 lines falling into the specified spectral range, in the Geisa case these are 4133 lines (look to the message above *Display-Modus*). A calculation over an extended spectral range (one quarter to the left and one quarter to the right) is done to consider any contributions which may result from the wings of lines lying outside the selected window width.

When the display modus (vertical axis) is set to *absorption coefficient* (default case) the graph represents the absorption of the gas composition in  $[cm^{-1}]$ .

Due to the limited resolution of the screen and the limited channel number used for this first calculation, the spectrum may look quantized. The step size for the calculation is automatically adapted to the pixel number of the screen. Under conditions, where the number of lines is larger than the pixel number, it is recommended to increase the channel number (see below).

### **Cursor Operation**

To observe some part of the spectrum in more detail and at an increased resolution new start and stop values can be chosen, as described before, or the spectral interval can be preselected with the cursor. In the latter case the cursor is moved to the desired start position (within the graphic screen) and the left mouse button is pressed. A vertical line (magenta colour) shows up and indicates this position. The exact start wavelength is also displayed by the cursor's x-coordinate in the left part of the control panel. Moving the mouse to the right and marking the stop position in the same way, the spectral interval is defined.

As an exercise select the interval from 1.99 to 2.035  $\mu$ m. A further click with the left mouse button to this interval activates the plot over the desired range on the magnified scale.

The original spectral range is recovered when pressing the right mouse button.

#### **Zoom Function**

A third possibility to determine or to modify the spectral range is to use the *Zoom* function. It is found at the lower right edge of the screen. When clicking on the '+ button', the resolution is further increased by a factor of two (half of the previous range), a click on the '- button' reduces the resolution by two. Pressing the < and > buttons shifts the spectrum by half the window width to the left and right, respectively. The **0** button recovers the original spectrum.

#### **Channel Number**

To obtain an overview over a wider spectral range with many narrow lines the standard resolution, which is adapted to the pixel number of the screen, may not be large enough. Under these conditions no supporting points or only a few points may fall within the spectral width of a transition. Nevertheless the MolExplorer is seeking for the maximum of the line and sets the channel closest to the center to this maximum value.

The resolution can be improved by activating the checkbox *channels* and increasing the number of channels used for the computation. This is quite beneficial for exported data used for high resolution plots, but also slightly improves the quality when regarding the spectra on the screen, even though the limiting resolution is determined by the pixel number of the screen.

Choose 4096 channels and again click on the *Calculate* button. Then the band structure should look as displayed by the following screen shot.



### 3.5 Display Modus

The MolExplorer works in five different display modes:

- Absorption Coefficient,
- Absorption,
- Line Positions,
- Line Strengths and
- Transmission.

They can be selected in the respective drop-down menu.

### **Absorption Coefficient**

This is the default modus when starting the program. The absorption coefficient  $[cm^{-1}]$  just represents the absorption over a propagation length of *1 cm*. It is found by summing up all the contributions of different lines in a spectral region as a function of frequency or wavelength.

**Line Shapes:** The different lines suffer from broadening effects which cause a spectral line spread and are described in chapter 7 in more detail. At regular atmospheric conditions collisional (or pressure) broadening is the dominating effect, while at low pressures and short wavelengths Doppler broadening can surpass this contribution.

The MolExplorer automatically determines the collision and Doppler broadening for each individual line and uses the respective line shape (a Lorentzian for collisions, a Gaussian for Doppler broadening and a Voigt profile in the intermediate case) to calculate the spectral absorption. During the computation a status line (above the gas input fields) indicates which line shape is applied. In the case of a Voigt profile larger channel numbers should be avoided, since for this shape a convolution of a Lorentzian and Gaussian profile has to be calculated for each transition.

A special line shape, derived from molecular response theory [10, 11], can be used, clicking on the check box *Response Time*. This theory considers the time response of molecules to come into thermal equilibrium with an external electric field, prevailing upon the molecules. This line shape is of relevance for lines with line widths comparable to the transition frequency (for details see chapter 7 and Ref. 10). This calculation modus is only effective, when the THz frequency scale is chosen. Typical values for the response time of light molecules are of the order of 0.1 - 0.5 ps.

For survey spectra with hundredths or thousands of lines and spectra with narrow line widths an individual line is only displayed by one or a few pixels on the screen. In this case the program does not distinguish between different line shapes, but for simplicity calculates with a Lorentzian. Nevertheless, the line intensity is well approximated by an empirical formula, which determines the maximum value of the real line shape (see chapter 7). As long as this calculation modus is applied, the status line indicates the message *Lorentz Approxim*.. If the spectral width of a line covers 6 or more channels, calculation with the true line shape is applied.

The displayed spectrum is always normalized to the maximum absorption coefficient within the selected spectral range. This maximum is displayed under the cursor position.

To determine the absorption coefficient at the center or in the wing of a line, the cursor is moved to the desired position and from the cursor display the absorption as well as the exact position on the wavelength or frequency scale can be read.

The vertical axis can be changed to a logarithmic scale when the checkbox Log Range is activated.

### Absorption

The absorption (dimensionless) is found by multiplying the absorption coefficient with the propagation length L [*cm*] of the radiation in the atmosphere or in a gas cell. All features of this display modus are identical with the previous modus. The path length can be changed in the respective input field.

### **Marker Function**

Together with the *Absorption* and *Absorption Coefficient* display modus a marker function can be activated, which is particularly helpful when a spectrum consisting of different gases or isotopologues is plotted to distinguish the different components and contributions. Each line position is indicated by a

marker which carries the color of the respective gas, and the marker length (or height) approximates (slightly dependent on the line shape) the maximum absorption of an individual line. This has the advantage that the true peak intensity of a line is depicted even under conditions when lines are overlapping or a limited resolution with only a few pixels across the line causes some arbitrary shape.

To convince yourself, set the marker and press the right mouse button. The original spectrum from  $1.9 - 2.1 \,\mu m$  appears, then select the interval from  $2.030 - 2.047 \,\mu m$  with the cursor. Now the lines of the three isotopes and their contributions can easily be identified. Also look at a further magnified scale using the *Zoom* (press two times +).



### **Double Plot**

In order to compare a new calculation of a spectrum with a previous one or to identify smaller changes in the spectrum, a double plot can be activated.

Set the checkbox *Double Plot*, click on *Calculate*, make your changes and calculate again. The white graph then represents the new calculation, the light blue curve shows the older run.

### **Line Positions**

A pure line spectrum is shown, when the display modus is switched to *Line Positions*. This mode is favorably used, to obtain an overview over a wide spectral range with many narrow lines.

The line spectrum is identical with the marker function: each molecular transition is represented by a single vertical line, where the line position reflects the transition frequency and the line length (or height) the maximum absorption coefficient at the center of the transition in  $[cm^{-1}]$ .

For very dense spectra where two or more lines can fall within one channel, the sum of the line heights is displayed.

#### Line Strengths

In this modus also a pure line spectrum is displayed, indicating the spectral line intensities (or line strengths)  $[cm^{-1}/(molecule \cdot cm^{-2})]$ , as they are stored in the HITRAN and GEISA database (for definition of the line intensity see chapter 7 and Ref. 9).

The spectral intensity is a key parameter, when calculating the spectrum. A minimum value can be specified to suppress lines with very small intensities or to restrict the number of lines for the computation. Coinciding lines falling within the same channel are also summed up.

### Transmission

The transmission modus calculates and displays the transmitted radiation being propagated through the atmosphere or a gas cell of length L [*cm*]. The path length can be changed in the respective input field. Different gas components can clearly be distinguished, when the marker is activated.

In the logarithmic mode the cursor position is also displayed in decibels.

### 3.6 Line Parameters

All relevant data of a transition which are stored in the HITRAN08 or GEISA-03 database can be displayed on the screen.

To select a specific line of interest, the cursor is moved to this line and marked by a double click with the left mouse button. A vertical and horizontal line appears for 1 s and indicates which line was marked and identified. For pressure shifted lines a second pair of dashed lines appears at the position of the unshifted frequency or wavelength, before the graphic screen changes to a white field in which all data of this line are listed.

For the definition of these parameters look at the HITRAN homepage http://www.hitran.com or GEISA homepage <u>http://ara.lmd.polytechnique.fr/</u> – subfolder Documentation, where you find the basic articles.

### 3.7 Parameter-File

The calculation and display of a spectrum requires a number of input data, e.g., the molecule and isotopologue choice, the partial and buffer gas pressure, or the spectral range and the display modus, which all have to be typed in. When a special parameter set shall be saved for later checks or recurring use, it is advantageous to store this configuration on a parameter file.

A click on the button *Write Parfile* at the left hand side of the panel opens a sub-window *Store under*, which asks for a file name. This parameter file can be stored in an arbitrary folder.

Reversely an existing file can be read, when clicking on the button Read Parfile.

Some examples of such parameter files are found on the program CD in the subfolder Parfiles. E.g. the file CO2-2µm-1hPa.txt, exactly reproduces the screen shot on page 8.

*Note:* parameter files from older versions of the MolExplorer may cause errors, since additional parameters are included. Files created with the Hitran version and read with the Geisa version or vice versa show a special message, when the gas or isotope is not present in the actual database.

### 3.8 Print and Export of Data

For fast inspection or preliminary documentation the spectrum as viewed on the monitor can be printed on a standard printer. Before starting the print, the printer installation and page to be printed may be checked. Open the Windows submenu *File* at the top line of the MolExplorer surface, control the printer setup, and then change to *Page View*. In this mode only rough inspection of the printed output is possible, but some further magnification of the page is possible. In addition to the spectrum the most important data used for the calculation are listed.

For high quality data representation the spectrum can be stored on a file, which is further processed by an external plot program. The first two lines contain information for a plot of the data, while the following lines and by this the file length is determined by the channel number used for the calculation. In the simples case the file consists of 2 columns, one for the frequency or wavelength scale and one for the absorption or transmission curve. With the marker function switched on or in the display modes *Line Position* and *Line Strength* for each gas an additional column which represents the respective line spectrum is generated.

Spectra displayed on a logarithmic scale on the screen are exported as non-logarithmic data. This has the advantage to use the logarithmic function of the plot programs. For automatic data processing a message (lin or log) is sent to the data file.

This file can be automatically processed, e.g., by a table calculation program like Excel or Xact and used for the graphic representation of the data. The standard file name is Specfile.txt and is sent to the folder, where the program was installed (default: c:\Programs\MolExplorer\).

Also a user defined path and file name for the exported data can be chosen under the Windows menu *File – Set Export Path* which, however, is only valid during the actual session.

### 4. Import of Spectral Data

The HITRAN and GEISA databases are well established standards for the reproduction of molecular spectra. Therefore it may be of interest to compare own measurements or calculations with one of these standards for the matter of calibration, identification of lines or the check of any inconsistencies.

### 4.1 Data-File

External spectra can be imported and read as dat- or txt-file. The first line has to have a special format containing two parameters for the representation of the data, while the following lines hold the xand y-values.

First Line:

1. parameter (x-axis type):	XAxisTypePCM	for wavenumbers
	XAxisTypeMYM	for wavelengths in µm
	XAxisTypeTHZ	for frequencies in THz
2. parameter (display modus):	Absorption	for an absorption measurement
	Transmission	for a measurement in transmission

For an absorption measurement on a wavelength scale, e.g., the first lines of the data-file look like:

XAxisTypeMYM	Absorption	or in the format	XAxisTypeMYM	Absorption
2.04130	51.86		2.045609e+000	6.481714e-006
2.04131	21.2		2.045612e+000	6.101706e-006
2.04132	38.08		2.045616e+000	5.753795e-006
2.04133	38.4		2.045620e+000	5.435443e-006

All data are separated by a space bar.

A click on the button *Import Data* opens the sub-window *Open File* and allows to load the data file. The program presumes a linear y-axis scale and a constant step width of the x-axis data. Having selected the desired file, the spectrum is automatically displayed on the screen as a red graph.

As an example import the data-file CO2-Measure.dat, which is found in the folder Parfiles on the CD. Make sure that the log-modus is switched off.

### 4.2 Comparison with Calculated Spectrum

To compare the imported spectrum with a calculation based on the HITRAN or GEISA database, the same steps have to be applied as known from a standard calculation. So, the gases and/or isoto-pologues, their partial pressures, the buffer-gas pressure and temperature have to be entered, while the spectral range, the abscissa type and display modus are already set by the imported spectrum. The computation is started by the *Check* button and displayed by a click on the *Calculation* button.

Alternatively a prepared parameter file can be loaded, which contains all information for a calculation, including the abscissa type, spectral range and display type. This parameter file can be loaded before or after importing the data file. E.g., read the parfile CO2-2.0µm-Air.txt from the folder Parfiles.

The y-axis of the data file is automatically adapted to the screen height, independent of the display modus and scaling. This moderates the display of imported data but prohibits comparison with the calculation on an absolute scale.

A click on the button *Fit Data* opens a submenu to fit the amplitude and background of the imported spectrum. A fit to the frequency or wavelength scale requires to enter the start and stop values via the submenu *Spectral Range* (click on respective radio button) and a new *Check*.

Part of the spectrum can be selected and displayed with the cursor function.

### 4.3 Parameter File

If the check box *Measurement* is activated, a parameter file can be saved, which additionally stores the path and name of the imported file as well as the fit parameters.

Reversely when this parameter file is read, the external spectrum is imported and compared with the simulated spectrum.

The screen shot below is an example for the imported spectrum CO2-Measure.dat as red graph together with a simulation (parfile CO2-2.0 $\mu$ m-Air-Fit.txt: 0.35 hPa CO<sub>2</sub>, 5 hPa H<sub>2</sub>O in air) as white line.



### 4.4 Data Export

With the check box *Measurement* activated the imported spectrum can be stored together with the calculated spectrum on the Specfile.txt for external processing of the data. The measurement appears in the last column of the data file and is scaled in units of the calculated spectrum. If only part of the original spectrum is displayed on the screen, also this part is exported. In order to adapt this spectrum to the new resolution, it is linearly interpolated between the original data points.

### 5. Atmospheric Calculation

The MolExplorer can be used to estimate the absorption and transmission losses of radiation in the atmosphere. The program calculates losses through a standard atmosphere [12] under the influence of Mie scattering and free-space-damping.

### 5.1 General Description

### **Propagation Geometry**

The propagation of electromagnetic radiation through the atmosphere is controlled by three parameters, the *Start Height,* the *Elevation Angle* and *Propagation Length.* These parameters determine the

altitude of the transmitter antenna above sea level in *km*, the direction of the beam with respect to the horizontal (or the normal to the earth radius) and the path length in *km*.

Since the beam spreads out over different altitudes above ground level, the absorption of the atmosphere has to be calculated for individual layers above the earth's surface as a function of pressure and temperature, and these contributions have to be summed up to the total absorption.

Absorption losses are considered up to an altitude of *86 km* above ground level. Then the air pressure has dropped down to less than *0.01 hPa*.



#### **Mie Scattering**

Mie scattering is considered as long as the beam is propagating in atmospheric layers below 10 km. At higher altitudes with pressures less than one quarter of the ground pressure and temperatures of about 216 K any scattering by ice crystals, droplets or pollutions is neglected.

At altitudes between sea level and 8 km a unique scattering coefficient is assumed which can be expressed by the surface visibility *V*. This quantity is defined as the path length (in units of *km*), over which 2% of the incoming light is transmitted at a wavelength of  $\lambda = 0.55 \ \mu m$ . Visual range measurements are daily reported at airports and weather forecast bureaus. For the wavelength dependence of the Mie scattering coefficient the empirical relation after Kruse et. al. (see Ref. 13 and chapter 7) was assumed.

In order to simulate any losses caused by a cloud layer, a further parameter, the cloud visibility, can be used, which takes into account scattering losses for altitudes between 8 and 10 km.

#### **Free-Space-Damping**

Transmission losses caused by the limited beam divergence and receiver antenna size are designated as free-space-damping. The MolExplorer computes transmission losses resulting from the diffraction limited propagation of the beam. For longer distances, when the beam diameter of the transmitted radiation is larger than the receiver antenna, the transmittance is proportional to the areas  $A_T$  and  $A_R$  of the transmitter and receiver antenna and inversely proportional to the path length and wavelength squared (see chapter 7.6).



### 5.2 Operation

### **Selection of Gases**

For the calculation of atmospheric losses first the composition of the atmosphere at ground level has to be specified. If for the spectral range of interest oxygen or nitrogen lines are expected, these gases

may be selected from the drop down menus of the gas input fields, and their partial pressures have to be keyed in. Otherwise these main constituents of the atmosphere can be considered as buffer gas, and only the other gases of interest with their partial pressures have to be specified, e.g., 0.35 hPa  $CO_2$ , 20 hPa  $H_2O$  and 0.001 hPa  $OH^+$ . Make sure that the sum of the partial pressures and the buffer gas pressure gives the overall pressure at ground level.

Atmospheric Parameter	rs	×
Start Height [km]	10	
Elevation Angle	-37	
Propagation Length [km]	16	Cancel · +
Surface Visibility [km]	20	Stop 5 Calculate
Cloud Visibility [km]	5	
Transmitter Diameter[cm]	5	Height Resolution
Detector Diameter[cm]	20	- · · · · · · · 50

For the variation of the pressure and temperature with altitude the standard atmosphere model is applied. Additionally, a uniform relative composition of the gases with height is assumed.

#### **Spectral Range and Display Modus**

Select the abscissa type (wavenumbers, frequencies or wavelengths) and the spectral range.

As display modus choose *Absorption* or *Transmission*. A calculation of the atmosphere is only possible in these modes.

#### **Atmospheric Parameters**

Open the Windows submenu *Extras* at the top line of the MolExplorer surface and click on *Atmosphere*. The sub-window *Atmospheric Parameters* opens and allows to control the most relevant parameters which are of importance for simulating the propagation of radiation.

The *Start Height* (in km) determines the position of the transmitter above ground level. Arbitrary values between zero and infinity can be typed in.

The *Elevation Angle* defines the direction of the beam with respect to the horizontal (or the normal to the earth radius). For increasing altitudes the angle has to be specified between 0 and 180°, for decreasing altitudes from 0 to -180°. If at negative angles the beam hits the surface, a message window appears and asks for new parameters.

The *Propagation Length* has to be specified in units of *km*. This value is also overtaken from the main control panel when leaving the sub-window, but then is displayed in *cm*.

Under bad weather conditions the *Surface Visibility* may be chosen between 0.1 and 3 km, under regular conditions between 5 and 20 km and at very good visual range larger 30 km.

The Cloud Visibility can vary between 0.05 and 2 km.

The *Transmitter* and *Detector Diameter* define the antenna areas of the transmitter and receiver, for which circular surfaces were assumed. Any losses due to free-space-damping can only be observed in the transmission modus.

If one of the visibilities is set to zero, the respective Mie scattering is switched off. Similarly, with zero transmitter or detector diameter the free-space-damping is switched off.

### **Height Resolution**

The layer thickness and by this the step width, over which the absorption is calculated as a function of pressure and temperature, is varying with altitude. So, the lower layers of the troposphere up to *11 km* are computed with the highest resolution. With the slide controller in the left position (1.0) this corresponds to a minimum increment of 100 m. From 11 to 20 km in this position the step width is 200 m, from 20 - 32 km: 400 m, from 32 - 47 km: 800 m and from 47 - 86 km: 1,600 m.

This dynamic resolution takes account of the fact, that higher layers contribute less to the resulting absorption, and on the other hand the computation time is significantly reduced.

For spectra with more than 10,000 lines it is recommended to decrease the *Height Resolution* and by this to increase the multiplier for the layer thickness (up to 20x) by shifting the slide controller to the right side. The actually calculated height is displayed in the lower status line of the screen.

### Parameter File

All parameters are stored on the parameter file and can be read from this file.

### **Example for Simulated Transmission**

A calculation with parameters as displayed in the upper sub-window and the main window is shown on this screen shot. This example is stored on the parfile Atmos-0.8-1.6µm-10km.txt, which is found in the subfolder Parfiles. Read this file, open the submenu *Extras-Atmosphere* and click on *Calculation*.



### 6. Instrument Function

Often measured spectra suffer from spectral broadening due to the limited resolution of a spectrometer. In order to compare such measurements with a calculated spectrum or to simulate any additional broadening, the MolExplorer provides two options to include additional broadening mechanisms.

One quite simple option is to add an additional line width to the calculated Doppler or collision broadening and by this to increase the overall spectral width of a line which then is computed as Gaussian, as Lorentzian or as convolution of these basic line shapes (depending on the ratio of the resulting Doppler to collision broadening).

The other option is to compute the mathematical folding of the calculated spectrum with an instrument function, which is characterized by its width and shape.

### Operation

Open the Windows submenu *Extras* at the top line of the MolExplorer surface and click on *Instrument Function*. The respective sub-window opens and displays a graphical user interface to specify the mode, the broadening profile and spectral width.

### **Additional Broadening**

In the default configuration the field *Additional Broadening* is selected. In this mode an additional contribution of Doppler or collision broadening can be specified by clicking on one of the radio buttons *Gauss* or *Lorentz*.

For a spectrum calculated in wavenumbers also the spectral width has to be entered in  $cm^{-1}$ . When switching to the wavelength or THz scale, the width is converted to *nm* or *GHz* respectively.

To start a calculation, click on the button Enable Folding.

#### Instrument Function

The option Instrument Function is activated when clicking on the respective Select button and the requested instrument profile.

Instrument Function	
Additional Broadening	Spectral Width 0.01 nm
C Gauss C Lorentz	Calculate Double Plot
Instrument Function	
Select	
C Gauss C Lorentz	C Airy • SI-Square C Rectangle
Enable Folding	OK Cancel

The convolution of a calculated spectrum with a Gaussian or Lorentzian gives similar results as in the previous case. However, it should be noticed that the folding procedure is restricted to the central part of the instrument function, while the distant wings are neglected. This was done to reduce the calculation time.

Since the instrument functions are more or less rapidly decreasing with increasing frequency detuning from resonance, different spectral intervals were chosen for the convolution (for details see chapter 7.7). So, for a Gaussian 5 full spectral widths are applied, for a Lorentzian and Airy function 10 widths, for the SI<sup>2</sup> 2 widths and the rectangle one width.

Due to the folding some part of the spectrum at the left and right margin may be cut off. This missing spectrum gets larger the more the convolution width covers the original spectrum.

The accuracy of the numerical folding is limited by the quantized channel resolution, which not only determines the line width of a transition, but can also strongly influence the intensity of a line. Therefore, most accurate calculations are performed with higher channel numbers.

If the marker function is activated, it should be noticed, that the marker lengths are renormalized to the folded spectrum and no longer represent the absolute line strengths. However, they still display the relative line intensities, and the color identifies the molecule or isotopologue.

### 7. Theory

In order to compute the transmittance of the atmosphere or a gas sample over a specified spectral region, it is necessary to consider all vibrational-rotational lines of the gas within this frequency range and to determine the total absorption coefficient as a function of frequency. This total absorption is the sum of the individual line absorption coefficients which on their part depend on four essential line parameters, the transition frequency  $v_{nn'}$  [cm<sup>-1</sup>], the spectral line intensity  $S_{nn'}$  per absorbing molecule  $[cm^{-1}/(molecule cm^{-2})]$ , the number density of molecules  $N[cm^{-3}]$ , and the line shape function g(v).

Since all data in the HITRAN08 or GEISA-03 database are specified in cgs-units, the following theoretical description relates to these units. At the end of this chapter a table with the relevant quantities in cgs- and SI-units is given.

### 7.1 Transition frequency

 $E_{n'}$ 

Molecular transitions between two states with energies  $E_{\eta}$  and  $E_{\eta'}$  [cm<sup>-1</sup>] are considered, where the index  $\eta$  denotes the lower and  $\eta'$  the upper state. The energy difference between these states defines the transition frequency in  $cm^{-1}$ 

$$\nu_{\eta\eta'} = E_{\eta'} - E_{\eta} \tag{1}$$

and determines the center position of a line. In the HITRAN and GEISA database all line-by-line data of a gas are systematically arranged due to their increasing transition frequencies.



Fig. 7.1: Two-level system, indicating a transition between states  $\eta$  and  $\eta'$ .

These frequencies may be shifted proportional to the air pressure  $p_{air}$  [*atm*] yielding a shifted frequency  $v_{nn'}^{p}$ :

$$v_{\eta\eta'}^{p} = v_{\eta\eta'} + \delta \cdot p_{air} \tag{2}$$

with  $\delta$  as the air-broadened pressure shift [*cm*<sup>-1</sup>/*atm*] at a reference temperature  $T_{ref} = 296K$  and reference pressure  $p_{ref} = 1$  *atm* (1 *atm* = 760 *Torr* = 1013.25 *mbar* = 1013.25 *hPa*). This parameter is transition dependent and stored in the database for each line. For molecules and lines for which no pressure shift coefficients are known the default value is  $\delta = 0$ .

#### 7.2 Spectral line intensity

The spectral line intensity  $S_{\eta\eta'} [cm^{-1}/(molecule \cdot cm^{-2})]$  (at  $T_{ref} = 296 \text{ K}$ ) of a vibrational-rotational transition is defined in radiative transfer theory [9] as

$$S_{\eta\eta'} = \frac{h v_{\eta\eta'}}{c} B_{\eta\eta'} \frac{N_{\eta}}{N} \left( 1 - \frac{g_{\eta}}{g_{\eta'}} \frac{N_{\eta'}}{N_{\eta}} \right),$$
(3)

where  $B_{\eta\eta'}[cm^3/(ergs \ s^2)]$  is the Einstein coefficient for induced absorption,  $N_\eta$  and  $N_{\eta'}[cm^{-3}]$  are the populations of the lower and upper states, respectively,  $g_\eta$  and  $g_{\eta'}$  are the state statistical weights, N [ $cm^{-3}$ ] is the molecular number density,  $c \ [cm/s]$  the speed of light in vacuum and h Planck's constant with  $h = 6.6262 \times 10^{-27} \ erg \ s = 6.6262 \times 10^{-34} \ J \ s.$ 

Eq. (3) may be derived considering an electromagnetic wave with spectral energy density  $\rho_{\nu}$  [*ergs/(cm<sup>3</sup> cm<sup>-1</sup>)*] which is interacting with molecules and causes induced transitions. According to energy conservation, changes in radiation are coupled to changes in the population of the involved states:

$$\frac{d\rho_{\nu}}{dt} = -c \left(\sigma_{\eta\eta'}(\nu)N_{\eta} - \sigma_{\eta'\eta}(\nu)N_{\eta'}\right)\rho_{\nu} = -c \sigma_{\eta\eta'}(\nu)N_{\eta} \left(1 - \frac{g_{\eta}}{g_{\eta'}} \frac{N_{\eta'}}{N_{\eta}}\right)\rho_{\nu} 
= -h \nu_{\eta\eta'} \left(B_{\eta\eta'}N_{\eta} - B_{\eta'\eta}N_{\eta'}\right)g(\nu)\rho_{\nu} = -h \nu_{\eta\eta'} B_{\eta\eta'} g(\nu) N_{\eta} \left(1 - \frac{g_{\eta}}{g_{\eta'}} \frac{N_{\eta'}}{N_{\eta}}\right)\rho_{\nu}$$
(4)

with  $\sigma_{\eta\eta'}(v)$  and  $\sigma_{\eta'\eta}(v)$  [*cm*<sup>2</sup>] as the induced absorption and emission cross sections related to each other and to the Einstein coefficients for induced absorption and emission  $B_{\eta\eta'}$  and  $B_{\eta'\eta}$  by

$$\sigma_{\eta'\eta}(v) = \frac{g_{\eta}}{g_{\eta'}} \sigma_{\eta\eta'}(v) = \frac{hv_{\eta\eta'}}{c} B_{\eta'\eta} g(v) = \frac{g_{\eta}}{g_{\eta'}} \frac{hv_{\eta\eta'}}{c} B_{\eta\eta'} g(v),$$
(5)

where g(v) is a normalized line shape function of the form

$$\int_{0}^{\infty} g(v) dv = 1.$$
(6)

The net absorption in Eq. (4) determined by the difference of induced absorption and emission processes, can also be expressed by an effective absorption cross section  $\overline{\sigma}_{\eta\eta'}(\nu)$  and referred to the molecular number density *N*:

$$\frac{d\rho_{\nu}}{dt} = -c\,\overline{\sigma}_{\eta\eta'}(\nu)\,N\,\rho_{\nu}\,,\tag{7}$$

which by comparison with Eq. (4) gives the effective cross section

$$\overline{\sigma}_{\eta\eta'}(\nu) = \frac{h\nu_{\eta\eta'}}{c} B_{\eta\eta'} \frac{N_{\eta}}{N} \left( 1 - \frac{g_{\eta}}{g_{\eta'}} \frac{N_{\eta'}}{N_{\eta}} \right) g(\nu) \,. \tag{8}$$

Integration of this expression over all frequencies results in an *integral* effective absorption cross section which then represents the spectral line intensity  $S_{\eta\eta'}$  (see Eq.(3)):

$$S_{\eta\eta'} = \int_{0}^{\infty} \overline{\sigma}_{\eta\eta'}(\nu) \, d\nu = \frac{h \, \nu_{\eta\eta'}}{c} B_{\eta\eta'} \frac{N_{\eta}}{N} \left( 1 - \frac{g_{\eta}}{g_{\eta'}} \frac{N_{\eta'}}{N_{\eta}} \right) \tag{9}$$

This is an appropriate quantity to describe the absorption strength of a transition independent of the homogeneous line broadening and line shape. It represents the area under the line shape, as shown in Fig. 7.2.



Fig. 7.2: For explanation of the spectral line intensity.

#### Temperature dependence of $S_{\eta\eta'}$

Since the state populations vary significantly with temperature, all line intensities  $S_{\eta\eta'}$  listed in the database, apply to the reference temperature  $T_{ref} = 296 \text{ K}$ . For other temperatures T they can be calculated assuming thermodynamic equilibrium. Then the population partition between states is governed by Boltzmann's statistics and leads to the relations

$$\frac{g_{\eta}}{g_{\eta'}}\frac{N_{\eta'}}{N_{\eta}} = \exp\left(-\frac{hc\,v_{\eta\eta'}}{kT}\right); \qquad \frac{N_{\eta}}{N} = \frac{g_{\eta}}{Q(T)}\exp\left(-\frac{hcE_{\eta}}{kT}\right). \tag{10}$$

 $E_{\eta}$  is the lower state energy [*cm*<sup>-1</sup>], *k* Boltzmann's constant with  $k = 1.38 \times 10^{-16} \text{ erg/K} = 1.38 \times 10^{-23} \text{ J/K}$ , and Q(T) the total internal partition sum given by

$$Q(T) = \sum_{\eta} g_{\eta} \exp\left(-\frac{hcE_{\eta}}{kT}\right).$$
(11)

While the first relation of Eq.(10) describes the relative population of the states  $\eta$  and  $\eta'$  as a function of temperature, the second determines the fraction of molecules in the lower state compared to the total population of all rotational-vibrational states. Substituting Eq. (10) and (11) in Eq. (9) at  $T_{ref}$  and introducing  $I_{a}$ , the natural terrestrial isotopic abundance, gives

$$S_{\eta\eta'}(T_{ref}) = \frac{h\nu_{\eta\eta'}}{c} B_{\eta\eta'} \frac{I_a g_{\eta}}{Q(T_{ref})} \exp\left(-\frac{hcE_{\eta}}{kT_{ref}}\right) \left(1 - \exp\left(-\frac{hc\nu_{\eta\eta'}}{kT_{ref}}\right)\right)$$
(12)

This is the definition as used in the HITRAN database [3] with  $S_{\eta\eta'}$  weighted according to the isotopic abundances given in the HITRAN file molparam.txt. The MolExplorer displays  $S_{\eta\eta'}$  in this form when choosing the *Line Strength* modus.

With reference to Eq. (12) the line intensity (or line strength)  $S_{\eta\eta'}(T)$  at temperature *T* can be calculated from  $S_{\eta\eta'}(T_{ref})$  by [3]

$$S_{\eta\eta'}(T) = S_{\eta\eta'}(T_{ref}) \frac{Q(T_{ref})}{Q(T)} \frac{\exp(-hcE_{\eta}/kT)}{\exp(-hcE_{\eta}/kT_{ref})} \frac{(1 - \exp(-hcv_{\eta\eta'}/kT))}{(1 - \exp(-hcv_{\eta\eta'}/kT_{ref}))}$$
(13)

The total internal partition sums are stored for each molecule and isotopologue in a separate HITRAN file (parsum.dat), which for calculations at temperatures different from  $T_{ref}$  must be available in the folder, where the Hitran08.par file is stored.

### 7.3 Absorption Coefficient

An effective absorption coefficient [ $cm^{-1}$ ], representing the net absorption between induced absorption and emission processes between the states  $\eta$  and  $\eta'$  of a molecule, is defined as (see also Eq. (7)):

$$\overline{\alpha}_{\eta\eta'}(\nu) = \overline{\sigma}_{\eta\eta'}(\nu) N, \qquad (14)$$

which according to Eqs. (8) and (9) can be written as

$$\alpha_{\eta\eta'}(\nu) = S_{\eta\eta'} N g(\nu) \tag{15}$$

with g(v) as the normalized line shape function describing the spectral line spread about the transition frequency.

Under conditions where molecules obey the universal gas equation, the number density  $N[cm^3]$  can be expressed by the partial pressure  $p_s[dyn/cm^2]$  of the gas:

$$p_{s}[dyn/cm^{2}] = NkT$$
<sup>(16)</sup>

or with  $p_s$  in [*atm*]:

$$p_{s}[atm] = 1.013 \times 10^{6} N k T$$
 (16a)

Eq. (15) then assumes the form

$$\overline{\alpha}_{\eta\eta'}(\nu) = S_{\eta\eta'} \frac{p_s}{kT} \frac{10^{-6}}{1.013} g(\nu).$$
(17)

#### **Collision broadening of spectral lines**

Under atmospheric conditions pressure broadening is the dominating process which determines the observed spectral line spread. The pressure broadened width  $\Delta v_{\eta\eta'}^{p}$  (FWHM) depends on two contributions, foreign gas broadening, caused by the air or other gases, and self-broadening of the gas itself. The resulting line width is calculated as

$$\Delta v_{\eta\eta'}^{p} = 2\gamma_{\eta\eta'}^{air}(p-p_{s}) + 2\gamma_{\eta\eta'}^{s}p_{s}, \qquad (18)$$

where  $\gamma_{\eta\eta'}^{air}$  and  $\gamma_{\eta\eta'}^{s}$  are the air-broadened and self-broadened halfwidth at half maximum (HWHM)  $[cm^{-1}/atm]$  at  $T_{ref} = 296 K$  and reference pressure  $p_{ref} = 1 atm$ , p is the overall pressure [atm] in the atmosphere or gas chamber and  $p_S$  the partial pressure [atm] of the gas. Both broadening coefficients are transition dependent and are stored in the database for each line. If other buffer gases than air or mixtures of gases are considered, their influence is assumed to be the same as that of air, because of the lack of respective cross broadening coefficients.

The temperature dependence of the pressure broadened line width  $\Delta v_{m'}^{p,T}$  is expressed as

$$\Delta v_{\eta\eta'}^{p,T} = \left(\frac{T}{T_{ref}}\right)^{-n_{\eta\eta'}} \Delta v_{\eta\eta'}^{p} = \left(\frac{T}{T_{ref}}\right)^{-n_{\eta\eta'}} \left(2\gamma_{\eta\eta'}^{air}(p-p_{s}) + 2\gamma_{\eta\eta'}^{s}p_{s}\right)$$
(19)

when  $n_{\eta\eta'}$  represents a transition dependent exponent of the line width, which is supposed to be equal for the air-broadened and self-broadened half-width.

As long as line widths comparable to the transition frequency (strongly broadened transitions in the *mm*- and *THz*-range) can be excluded, collision broadened lines are well represented by a Lorentzian line shape function:

$$g_{L}(\nu) = \frac{\Delta v_{\eta\eta'}^{p,T} / 2\pi}{\left(\nu - v_{\eta\eta'}^{p}\right)^{2} + \left(\Delta v_{\eta\eta'}^{p,T} / 2\right)^{2}}$$
(20)

satisfying Eq. (6). The absorption coefficient, Eq. (17), then assumes the form:

$$\overline{\alpha}_{\eta\eta'}(\nu, p, T) = S_{\eta\eta'}(T) \times \frac{p_s}{kT} \frac{10^{-6}}{1.013} \times \frac{\Delta v_{\eta\eta'}^{p, T} / 2\pi}{\left(\nu - v_{\eta\eta'}^p\right)^2 + \left(\Delta v_{\eta\eta'}^{p, T} / 2\right)^2}.$$
(21)

#### **Doppler Broadening**

At low pressures as well as at high transition frequencies (visible and near infrared) and high temperatures Doppler broadening may exceed the pressure broadening and determine the remaining line broadening.

The normalized Doppler line shape function, satisfying Eq. (6), has the form:

$$g_{D}(v) = \frac{1}{v_{\eta\eta'}} \left(\frac{mc^{2}}{2\pi k T}\right)^{1/2} \exp\left(-\frac{mc^{2}}{2kT} \frac{(v - v_{\eta\eta'})^{2}}{v_{\eta\eta'}^{2}}\right) = \frac{2\sqrt{\ln 2}}{\sqrt{\pi} \Delta v_{D}} \exp\left(-\frac{(v - v_{\eta\eta'})^{2}}{(\Delta v_{D}/2)^{2}} \ln 2\right)$$
(22)

with the Doppler line width  $\Delta v_D$  (FWHM)

$$\Delta v_D = 2v_{\eta\eta'} \left(\frac{2kT}{mc^2} \ln 2\right)^{1/2} = 7.16 \cdot 10^{-7} \times v_{\eta\eta'} \sqrt{T/M} , \qquad (23)$$

where *m* is the molecular mass [g] and *M* the molecular weight.

Therefore, under conditions, when  $\Delta v_{\eta\eta'}^{p,T} \ll \Delta v_D$ , the absorption coefficient turns into

$$\overline{\alpha}_{\eta\eta'}(\nu, p, T) = S_{\eta\eta'}(T) \times \frac{p_s}{kT} \frac{10^{-6}}{1.013} \frac{2\sqrt{\ln 2}}{\sqrt{\pi} \,\Delta \nu_D} \times \exp\left(-\frac{(\nu - \nu_{\eta\eta'})^2}{(\Delta \nu_D / 2)^2} \ln 2\right).$$
(24)

#### **Voigt Profile**

Under circumstances where pressure broadening is comparable to Doppler broadening, the correct absorption profile is computed as the mathematical folding of the two line shape functions  $g_L(v)$  and  $g_D(v)$  yielding the Voigt profile:

$$g_{V}(v) = \int_{0}^{\infty} g_{D}(v') \cdot g_{L}(v - v') dv'$$

$$= \frac{\sqrt{\ln 2}}{\pi \sqrt{\pi}} \frac{\Delta v_{\eta\eta'}^{p,T}}{\Delta v_{D}} \int_{0}^{\infty} \exp\left(-\frac{(v' - v_{\eta\eta'}^{p})^{2}}{(\Delta v_{D}/2)^{2}} \ln 2\right) \cdot \frac{1}{(v - v')^{2} + (\Delta v_{\eta\eta'}^{p,T}/2)^{2}} dv'$$
(25)

This line shape is applied as long as the inequality  $0.1 \le (\Delta v_D / \Delta v_{\eta\eta'}^{p,T}) \le 10$  for a spectral line is satisfied.

#### **Molecular Response Theory**

In the *mm*- and *THz*-range the line width of a transition caused by collisions can be comparable to the transition frequency of a line. Under these conditions the line shape can no longer be described by a standard Lorentzian, but is much better approximated by a shape derived from molecular response theory [10, 11]. This theory introduces a finite time, the response time, which molecules require to come into thermal equilibrium with an external field in the presence of molecular collisions. It is a unification of the classical collision theories of Lorentz and van Vleck-Weisskopf, where the response time  $\tau_c$  acts as a control parameter, which for large values (typically > 10 ps) already well reproduces a Lorentzian and for  $\tau_c = 0$  gives a van Vleck-Weisskopf line shape.

The general absorption line shape function is given by [10]:

$$g_{R}(\nu) = \frac{\Delta v_{\eta\eta'}^{p,T} / 2\pi}{\left(\nu - v_{\eta\eta'}^{p}\right)^{2} + \left(\Delta v_{\eta\eta'}^{p,T} / 2\right)^{2}} f^{+} - \frac{\Delta v_{\eta\eta'}^{p,T} / 2\pi}{\left(\nu + v_{\eta\eta'}^{p}\right)^{2} + \left(\Delta v_{\eta\eta'}^{p,T} / 2\right)^{2}} f^{-}$$
(26)

with the switching functions

$$f^{\pm} = 1 - \frac{v_{\eta\eta'}^{p} \mp v}{v_{\eta\eta'}^{p}} \frac{1 + \pi \cdot \Delta v_{\eta\eta'}^{p,T} \cdot \tau_{c}}{1 + 4\pi^{2} (v_{\eta\eta'}^{p} \mp v)^{2} \tau_{c}^{2}}.$$
(27)

The absorption coefficient then assumes the form:

$$\overline{\alpha}_{\eta\eta'}(\nu, p, T) = S_{\eta\eta'}(T) \times \frac{p_s}{kT} \frac{10^{-6}}{1.013} \times \frac{\nu}{\nu_{\eta\eta'}^p} g_R(\nu).$$
(28)

Note that different to Eq.(21) this expression contains an additional term  $v/v_{\eta\eta'}^p$ . Therefore, in comparison to a standard Lorentzian shape the absorption spectra in the far infrared are modified due to this term, the second resonance term for "negative frequencies" and the switching functions  $f^{\pm}$ ,

which in the limit  $1 \ll 4\pi^2 \left( v_{\eta\eta'}^p \mp v \right)^2 \tau_c^2$ ,  $f^{\pm} \rightarrow 1$ , and for  $1 \gg 4\pi^2 \left( v_{\eta\eta'}^p \mp v \right)^2 \tau_c^2$ ,  $f^{\pm} \rightarrow \pm v / v_{\eta\eta'}^p$ .

#### 7.4 Line Spectrum

For plots over a wide spectral range with narrow lines it may be advantageous to represent a molecular transition by a single vertical line and not the full line shape. In this case the line position reflects the transition frequency and the line length (or height) the maximum absorption at the center of the transition.

For collisional broadening (Lorentzian line shape) the maximum absorption is found from Eq. (21):

$$\alpha_{\eta\eta'}^{0}(\nu, p, T) = S_{\eta\eta'}(T) \frac{p_s}{kT} \frac{10^{-6}}{1.013} \frac{2/\pi}{\Delta v_{\eta\eta'}^{p,T}}.$$
(29)

If Doppler broadening is the dominating process, from Eq. (24) it is found:

$$\alpha_{\eta\eta'}^{0}(\nu, p, T) = S_{\eta\eta'}(T) \frac{p_s}{kT} \frac{10^{-6}}{1.013} \frac{2\sqrt{\ln 2}}{\sqrt{\pi} \, \Delta \nu_D} \,. \tag{30}$$

When the line shape is represented by a Voigt profile, the exact peak value can only be derived by numerical integration. An acceptable approximation is achieved by the expression

$$\alpha_{\eta\eta'}^{0}(\nu, p, T) = S_{\eta\eta'}(T) \frac{p_{s}}{kT} \frac{10^{-6}}{1.013} \frac{2\sqrt{\ln 2}}{\pi\sqrt{\pi}} \times \left( (\ln 2/\pi) (\Delta v_{\eta\eta'}^{p,T})^{2} + 1.25 \left[ 1 - \left( \frac{\Delta v_{\eta\eta'}^{p,T}}{\Delta v_{\eta\eta'}^{p,T} + \Delta v_{D}} \right)^{1.55} \right] \sqrt{\ln 2/\pi^{3}} \Delta v_{\eta\eta'}^{p,T} \Delta v_{D} + (\Delta v_{D}/\pi)^{2} \right]^{-1/2},$$
(31)

which in the limiting cases agrees with the Lorentzian or Doppler results. The line spectrum is shown on the screen together with the absorption spectrum, when the marker function is set. Eq. (31) is also used to calculate the maxima in the *Lorentz Approximation* modus.

#### 7.5 Transmission

Radiation with an input intensity  $I_0$  is propagating through the atmosphere or a gas cell of length L. According to Lambert-Beer's law the intensity drops down as:

$$I(\nu, L) = I_0 \exp[-\alpha_{\eta\eta'}(\nu)L].$$
 (32)

Then the transmission of the gas over this length is given by:

$$T(\nu, L) = \frac{I(\nu, L)}{I_0} = \exp[-\overline{\alpha}_{\eta\eta'}(\nu)L].$$
(33)

#### 7.6 Atmospheric Calculation

For the calculation of atmospheric absorption and transmission losses a standard atmosphere [12] is assumed. These calculations include Mie scattering and free-space-damping.

#### **Propagation Geometry**

The propagation of a beam through the atmosphere is described by the three parameters, the *Start Height*  $h_0$ , the *Elevation Angle*  $\varphi$  and the *Propagation Length L* (see Fig. 7.3).

#### **Atmospheric Absorption**

Since the absorption is changing with altitude h(z) and by this over the beam path z as a function of pressure and temperature, the overall absorption A is found as the integral of the absorption coeffi-

cient  $\overline{\alpha}_{\eta\eta'}^{i}(\nu, p, T)$  of a transition  $\eta \rightarrow \eta'$  in a gas *i* over the path length *L* and summed over all transitions and gases:

$$A(\nu,L) = \sum_{n} \int_{0}^{L} \overline{\alpha}_{\eta\eta'}(\nu, p(h), T(h)) \, dz \,.$$
(34)

Here *n* represents the sum over all transitions and gases.

Since the MolExplorer computes the absorption coefficient for a mixture of gases at specified partial pressures and temperatures, in accordance with Eq. (34) the overall absorption is derived by calculating the absorption coefficient for an atmospheric layer at altitude h with the respective temperature and pressure at this height, then multiplying this with the beam path in the layer and summing over all layers involved.

The relative composition of the most relevant gases can be assumed to be constant over the atmosphere. Only light gases like  $H_2$  and He may accumulate in higher altitudes, and  $O_3$  is found with a varying concentration between 12 and 50 km with a maximum around 25 km.



Fig. 7.3: Propagation of the beam through atmospheric layers.

The International Civil Aviation Organization has defined a standard atmosphere for aeronautics, which assumes

- a dry gas (relative humidity = 0%),
- with constants as global average values at sea level: air temperature  $T_0 = 288.15 \text{ K} (15 \text{ °C})$ , air pressure  $p_0 = 1013.25 \text{ hPa}$ ,
- with a vertical temperature change from 0-11 km: - 6.5 K/km (linear decrease with height), from 11-20 km: 0 K/km (no temperature change), from 20-32 km: 1.0 K/km (linear increase with height), from 32-47 km: 2.8 K/km (linear increase with height), from 47-86 km: - 2.145 K/km (linear decrease with height),

and pressures at
 h = 0 km: 1013.25 hPa,
 h = 11 km: 226.32 hPa.

h = 20 km: 54.75 hPa, h = 32 km: 8.68 hPa, h = 47 km: 1.10 hPa, h = 86 km: 3.73 $\cdot$ 10<sup>3</sup> hPa.

So, the temperature as a function of height can be described as:

$$T(h) = T(h_0) + a \cdot (h - h_0).$$
(35)

With this linear temperature variation within one of these regions, each of which is characterized by a specific coefficient *a*, the pressure variation as a function of height for  $a \neq 0$  is given by

$$p(h) = p(h_0) \left( 1 - \frac{a(h - h_0)}{T(h_0)} \right)^{\frac{M \cdot g}{R \cdot a}},$$
(36)

with M = 0.02896 kg/mol as the molar mass of the atmosphere,  $g = 9.807 \text{ m/s}^2$  as the earth's gravitational acceleration and R = 8.314 J/K/mol as the universal gas constant. With a = -0.0065 K/m, e.g., the exponent in Eq. (36) has the value 5.2559.

For the simple case a = 0 the standard barometric height formula

$$p(h) = p(h_0) e^{-(h-h_0)/H_s}$$
(37)

holds with  $H_S = 6.3421 \text{ km}$  as the scale height at an altitude of  $h_0 = 11 \text{ km}$ . For the higher altitudes from 20 to 86 km the pressure variation within one region was assumed to change linearly with height. Absorption losses for altitudes larger than 86 km above ground level are neglected. Then the air pressure has dropped down to less than 0.01 hPa.

With this pressure and temperature variation the absorption coefficient is calculated for an atmospheric layer at height *h* and width  $\Delta h$ . This coefficient is multiplied with the path length  $\Delta L$  in the layer, and finally it is summed over all partial absorptions.

To restrict the computation labor, from 0 - 11 km the minimum layer thickness was assumed to be:  $\Delta h = 100 \text{ m}$ , from 11 - 20 km:  $\Delta h = 200 \text{ m}$ , from 20 - 32 km:  $\Delta h = 400 \text{ m}$ , from 32 - 47 km:  $\Delta h = 800 \text{ m}$  and from 47 - 86 km:  $\Delta h = 1.6 \text{ km}$ . The individual step widths can further be increased by a slide controller (*Height Resolution*) up to 20 times.

The path lengths  $\Delta L$  are individually determined for each atmospheric layer by trigonometric relations, dependent on the geometric conditions, i.e. the actual position, height, direction and layer thickness.

#### Mie Scattering

Mie scattering of particles larger than or equal to the wavelength of the radiation is considered as long as the beam is propagating in atmospheric layers below 10 km. At higher altitudes any scattering by ice crystals, droplets or pollutions is neglected.

The Mie scattering coefficient  $\alpha_M$  can be expressed in terms of the visibility *V*, which is defined as the path length (in units of *km*), over which 2% of the incoming light is transmitted at a wavelength of  $\lambda = 0.55 \ \mu m$ . The frequency or wavelength dependence of  $\alpha_M$  is given by the empirical formula [13]

$$\alpha_M(\lambda) = \frac{3.91}{V} \left( \frac{0.55}{\lambda[\mu m]} \right)^q \tag{38}$$

with  $\lambda$  in  $\mu m$  and  $q = 0.585 \cdot V^{1/3}$  for  $V \le 6$  km or q = 1.3 for medium visibility.

At an altitude between sea level and 8 km a unique visual range, the surface visibility  $V_{S}$ , and therefore a fixed scattering coefficient  $\alpha_{MS}$  is assumed.

For altitudes between 8 and 10 km another coefficient  $\alpha_{MC}$  with the cloud visibility  $V_C$  is used, which takes into account scattering losses by a cloud layer.

The total Mie scattering loss is the sum of both contributions

$$S(\nu, L) = \alpha_{MS} \cdot L_S + \alpha_{MC} \cdot L_C \tag{39}$$

where  $L_s$  and  $L_c$  represent the paths of a beam in the two regions.

Mie scattering is displayed as a broad background together with the molecular absorption in the display modes *Absorption* or *Transmission* as

$$A_{T}(v,L) = A(v,L) + S(v,L).$$
(40)

$$T_T(v,L) = \exp[-(A(v,L) + S(v,L))].$$
(41)

#### Free-Space-Damping

Free-space-damping accounts for transmission losses caused by the finite beam divergence and limited receiver antenna size. The MolExplorer computes transmission losses resulting from the diffraction limited propagation of a Gaussian beam. The beam diameter at distance *L* from the transmitter is given by:

$$D(L) = D_T \left[ 1 + \left(\frac{4\lambda L}{\pi D_T^2}\right)^2 \right]^{1/2}$$
(42)

with  $D_T$  as the beam diameter or waist at the transmitter antenna.

When the beam diameter D(L) gets larger than the receiver antenna diameter  $D_R$ , only part of the transmitted power is caught by the receiver (see Fig. 7.4). The ratio of received to transmitted power  $P_R / P_T$  defines the transmittance caused by diffraction losses. For a Gaussian beam profile with beam radius *r* this is

$$T_D(L) = \frac{P_R}{P_T} = \frac{2 \cdot D_R^2}{D^2(L)} \cdot e^{-8r^2/D^2(L)} \approx \frac{D_R^2}{D^2(L)} = \frac{D_R^2}{D_T^2} + \left(\frac{4\lambda L}{\pi D_T}\right)^2,$$
(43)

where the approximation in Eq. (42) expresses the average over the beam cross section.



Fig. 7.4: Free-space-damping

For longer distances  $T_D(L)$  is proportional to the areas  $A_T$  and  $A_R$  of the transmitter and receiver antenna and inversely proportional to the path length and wavelength squared.

The total losses in transmission are given by the product of Eqs. (41) and (43).

### 7.7 Instrument Function

The MolExplorer provides two options to include an additional broadening which may be caused by the limited resolution of a spectrometer.

#### Additional Broadening

One option is to simply add an additional line width to the calculated Doppler or collision broadening and by this to increase the overall spectral width.

Assuming an additional spectral width  $\Delta v_a$  given by some broadening mechanism, in the Gaussian case this width together with the Doppler width  $\Delta v_D$  as calculated by the program, gives a new total Doppler width  $\Delta v_{D,a} = \Delta v_D + \Delta v_a$ . If this width satisfies the relation  $(\Delta v_{D,a} / \Delta v_{\eta\eta'}^{p,T}) > 10 (\Delta v_{\eta\eta'}^{p,T} - \text{pressure broadened line width})$ , the line is represented by a pure Gaussian with spectral width  $\Delta v_{D,a}$  (see Eq.(22)). For the Lorentzian case the width  $\Delta v_a$  together with the pressure width  $\Delta v_{\eta\eta',a}^{p,T}$  form the total pressure width  $\Delta v_{\eta\eta',a}^{p,T} = \Delta v_{\eta\eta'}^{p,T} + \Delta v_a$ , and under conditions that the inequality  $(\Delta v_{\eta\eta',a}^{p,T} / \Delta v_D) > 10$  is satisfied, the MolExplorer calculates with a pure Lorentzian shape of width  $\Delta v_{\eta\eta',a}^{p,T}$ . In the intermediate case  $0.1 \le (\Delta v_{D,a} / \Delta v_{\eta\eta'}^{p,T}) \le 10$  or  $0.1 \le (\Delta v_D / \Delta v_{\eta\eta',a}^{p,T}) \le 10$  the line shape is calculated as Voigt profile.

#### **Instrument Functions**

The other option is to compute the convolution of the calculated spectrum with an instrument function. In this case the spectrum exists as an array of length N (channel number), and each of these channels is multiplied and summed over n channels of the instrument function.

Five different profiles can be applied as instrument function:

Gauss-function:

$$f_D(\nu) = \exp\left(-\frac{(\nu - \nu_0)^2}{(\Delta \nu_a / 2)^2} \ln 2\right)$$
(44)

Lorentz-function:

$$f_{L}(\nu) = \frac{1}{\left[2(\nu - \nu_{0})/\Delta\nu_{a}\right]^{2} + 1}$$
(45)

Airy-function:

$$f_A(\nu) = \frac{(1-R)^2}{(1-R)^2 + 4R\sin^2((1-R)/\sqrt{R}(\nu-\nu_0)/\Delta\nu_a)}$$
(46)

SI<sup>2</sup>-function:

$$f_{S}(\nu) = \frac{\sin^{2}(\pi(\nu - \nu_{0}) / \Delta \nu_{a})}{\pi^{2}(\nu - \nu_{0})^{2} / \Delta \nu_{a}^{2}}$$
(47)

Rectangle-function:

$$f_{R}(v) = \begin{cases} 1 & \text{for } -\Delta v_{a}/2 \le (v - v_{0}) \le \Delta v_{a}/2 \\ 0 & \text{for } |v - v_{0}| > \Delta v_{a}/2 \end{cases}$$
(48)

These five profiles are displayed in Fig. 7.5. With a reflection factor R = 0.95 as typically used in a Fabry-Perot interferometer, the Airy function is almost completely identical with a Lorentzian over the spectral range shown in Fig. 7.5.



Fig. 7.5: Comparison of different instrument functions with identical halfwidths  $\Delta v_a$ .

In order to speed up the computation time, the folding procedure is restricted to the central part of the instrument function.

Since these functions differently pass off with increasing frequency detuning, different spectral intervals are chosen for a convolution. So, for a Lorentzian and Airy function at least 10 spectral widths are required and for a Gaussian 5 widths are used, while for an Sl<sup>2</sup>-function 2 widths (between the first zero points) and for the rectangle only one width is necessary.

Quantity	symbol	Cgs-units	SI-units
Energy	E	1 erg = 1 dyn cm	10 <sup>-7</sup> J
			1 eV = 1.602×10 ° J
Force	F	$1 \text{ dyn} = 1 \text{ g cm/s}^2$	10 <sup>-3</sup> N
	•	10⁵ dyn	1 N
Drocouro	2	$1 \text{ dyn/cm}^2 = 0.987 \times 10^{-6} \text{ atm}$	0.1 Pa
Flessule	ρ	$1.013 \times 10^{6} \text{ dyn/cm}^{2} = 1 \text{ atm}$	1.013 bar = 1013 hPa
dipole moment	μ	1 Debye	3.336×10 <sup>-30</sup> A s m
speed of light in vacuum	С	2.99792458×10 <sup>8</sup> m/s	2.99792458×10 <sup>10</sup> cm/s
Planck's constant	h	6.6262×10 <sup>-27</sup> erg s	6.6262×10 <sup>-34</sup> J s
Boltzmann's constant	k	1.38062×10 <sup>-16</sup> erg/K	1.38062×10 <sup>-23</sup> J/K
Term energy	$E_\eta$	1 cm <sup>-1</sup> = 1.9864×10 <sup>-16</sup> erg	1.9864×10 <sup>-23</sup> J
Frequency	$\mathcal{V}_{\eta\eta'}$	1 cm <sup>-1</sup>	2.9979×10 <sup>10</sup> Hz
number density	Ν	1 cm <sup>-3</sup>	10 <sup>6</sup> m⁻³

Table 1: Physical constants and conversion of units.

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